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(54) Title: EASY-OPEN PACKAGING (57) Abstract A laminate fabricated from a film or a sheet capable of forming peel seals suitable for vertical form/fill/seal packaging, which is made from a blend of an ethylene polymer, a metallocene-made polyethylene and a poly-1-butene polymer.		

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DESCRIPTIONEASY-OPEN PACKAGINGTechnical Field

5 This invention relates to a heat sealable wrapping or packaging film which is capable of forming a peelable seal having improved hot tack strength for vertical form/fill/seal packaging. Particularly, this invention relates to a film, a sheet or a laminate structure fabricated from a blend of an ethylene polymer made by a conventional catalyst, a metallocene-made polyethylene, 10 and a butene-1 homopolymer or copolymer. The seal is achievable either between two films of this kind or between one film of this kind and a rigid container without the need for an adhesive between this film and the container.

Background Art

15 A peelable seal is defined to be a seal or joint between two films produced by heat sealing or impulse sealing. The joint thus formed having sufficient peel strength, the property of being able to open in the original plane of joining of the two films by the action of a pulling force, without 20 tearing occurring in the material of the two films used to make up the joint. For the purposes of the present invention, the peelable seal must possess a mechanical resistance (peel strength) sufficient to maintain the wholeness and the tight-seal properties of the packing and wrapping during storage and 25 transport until such time as the packing or wrapping is opened by the user of the article. The mechanical resistance of the peelable seal must be low enough to permit ready manual opening of the joint, i.e., without the use of any auxiliary instrument.

30 This invention relates to a blend, and a method for making a blend usable in a flexible film package. This invention also relates to a film and/or a laminate which are characterized by a nearly constant peel strength over an extended heat seal temperature range and by being peelable. The term peelable refers to a film having seal failure which occurs primarily at the 35 interface of the sealing surface, and not by film tearing. The blends, films, and/or laminates of the present invention permit the manufacture of a more consistent finished product, having a

seal of predictable and constant peel strength, in spite of inevitable variations in the heat seal temperatures used in the production of such packages.

In the past, many variations of thermoplastic materials have been employed in the manufacture of films capable of forming peelable seals. Poly-1-butene homopolymer or copolymers, low density polyethylenes made by conventional catalysts, and low density polyethylenes made by metallocene catalysts each has certain hot tack strength. However, each of these polymers by itself exhibits a seal strength which is too strong and thus unsuitable for making peelable seals.

Blends of polyethylene homopolymers or copolymers with poly-1-butene polymers have been used commercially for making horizontal form/fill/peel seals. However, it lacks the required hot tack strength, that is the seal strength at elevated temperatures for vertical packaging. Hot tack strength is a critical property in the vertical form/fill/seal packaging. Vertical form/fill/seal packaging involves first sealing the bottom portion of the packaging films/laminates, such as bags, under an elevated temperature. This is immediately followed by filling the material to be packed, such as food, into the packaging films/laminates such as bags by "gravity", while pushing hot air downwardly into the bags. The top portion of the bag is then sealed with heat. In order to provide sufficient seal strength in vertical form/fill/seal packaging, the polymeric peel seal films must have sufficient seal strength at elevated temperatures (hot tack strength) so that the seals would not break during a vertical form/fill/seal packaging process.

There has been a long felt need for a blend having the required peel strength for use in peelable packaging seal, while having the required hot tack strength for use in certain applications such as vertical form/fill/seal packaging.

Disclosure of the Invention

It has now been found that certain properties including hot tack strength may be improved by fabricating films or sheets from blends having (i) 15-85 weight percent of an ethylene polymer made by a conventional catalyst, (ii) from about 10% to

about 70 weight percent of a metallocene-made polyethylene and (iii) from about 5 percent by weight to about 55 percent by weight of butene-1 homopolymer or copolymer. Such films or sheets are bonded to a substrate (or backing material) by coextrusion or extrusion lamination.

Brief Description of the Drawing

The drawing illustrates that the hot tack strengths of the present polymeric blends with LDPE (low density polyethylene made by a conventional Ziegler-Natta Catalyst), PB (poly-1-butene) and mLDPE (low density polyethylene made by a metallocene catalyst) are improved over a blend of LDPE and PB without mLDPE.

Detailed Description of the Invention

While the present invention is described in connection with the preferred embodiments, it will be understood that it is not intended to limit the invention to those embodiments. On the contrary, it is intended to cover all alternatives, modifications, and equivalents as may be included within the spirit and scope of the invention as defined by the appended claims.

The present invention is directed to a composition for producing a peelable heat seal film or sheet suitable for vertical form/fill/seal packaging comprising (i) from about 15 wt% to about 85 wt.%, specifically from about 35 wt.% to about 80 wt.%, more specifically from about 55 wt% to about 70 wt.%, of an ethylene polymer made by a conventional catalyst (ii) from about 10 wt.% to about 70 wt.%, specifically from about 20 wt.% to about 50 wt.%, more specifically from about 25 wt.% to about 45 wt.%, of a metallocene-made polyethylene, and (iii) from about 5 wt.% to about 55 wt.%, specifically from about 10 wt.% to about 40 wt.%, more specifically from about 15 wt.% to about 30 wt.% of a butene-1 homopolymer or copolymer. The weight percentages used herein are all based on the total weights of the blends.

The present invention is also directed to a film or a sheet made from the afore-mentioned blend. A film or sheet made from said blend, could be laminated with backing materials (or substrates), sealed to itself or to a rigid container at a heat sealing temperature of between about 160°F and about 500°F, as

determined at sealing jaws, affords a peel strength of between about 0.5 to about 8.0 pounds per inch, specifically from about 1.0 to about 6.0 pounds per inch, more specifically between about 1.5 to about 4.0 pounds per inch between the backing material
5 and a rigid container. A film or a sheet made from said blends also affords a hot tack strength of from about 1.0 about 4.0 newton/15 mm, specifically from about 1.5 to about 3.5 Newton/15 mm, more specifically from about 2.0 to about 3.0 Newton/15 mm.

This invention is also directed to a laminated film,
10 adapted for producing a material for making a container lid and a heat sealing film made from a blend of the above-mentioned composition. The laminated film has utility for achieving at a sealing temperature of about 160°F and about 500°F, as determined at sealing jaws, a peel strength of between about 0.5 to about
15 8.0 pounds per inch, specifically from about 1.0 to about 6.0 pounds per inch, more specifically between about 1.5 to about 4.0 pounds per inch between the backing material and a rigid container. A film or a sheet made from said blends also affords a hot tack strength of from about 1.0 about 4.0 Newton/15 mm,
20 specifically from about 1.5 to about 3.5 Newton/15 mm, more specifically from about 2.0 to about 3.0 Newton/15 mm.

The term ethylene polymer made by a conventional catalyst refers to any polyethylene homopolymer, any ethylene- α -olefin copolymer, or any ethylene-unsaturated ester copolymer
25 made by a conventional catalyst such as a Ziegler-Natta catalyst. The polyethylene homopolymer or ethylene- α -olefin copolymer is made by a conventional Ziegler-Natta Catalyst of Group IV-VI transition metal, specifically by a vanadium metal compound, a zirconium metal compound or a titanium halide (TiCl_4 or TiCl_3),
30 optionally supported by magnesium halide, with an aluminum trichloride or alkyl aluminum (halides) cocatalyst. Suitable polyethylene include all commercially available ethylene homopolymers, ethylene- α -olefin copolymers, such as a high density polyethylene (HDPE) with density of more than 0.94 g/cc,
35 a medium density polyethylene with density of 0.93 to 0.94 g/cc, a low density polyethylene (LDPE) with density of less than 0.93 g/cc, or a linear low density polyethylene (LLDPE). As a

specific embodiment of the present invention, the polyethylene is a LDPE, more specifically LDPE 2500 or LDPE 2500FA, which may contain certain additives, available from Shell Chemical Company located at London England.

5 The ethylene-unsaturated ester copolymer refers to any copolymer made by copolymerizing of ethylene and an unsaturated ester using a conventional catalyst. The unsaturated esters are esters of (1) carboxylic acids having 1-8 carbon atoms, and (2) an alcohol having 2-8 carbon atoms and containing at least one
10 double bond. Non-limiting examples of suitable unsaturated ester include vinyl acetate, vinyl butyrate, vinyl formate, etc. As a specific embodiment of the present invention, the DuPont Alathon® 3159 polyethylene-vinyl acetate is used. These ethylene-unsaturated ester copolymers are polymerized by conventional
15 process. An illustrative non-limiting example of the conventional process involves the used of any conventional Ziegler-Natta catalyst(s).

 The metallocene-made ethylene polymer referred to herein are any ethylene homopolymer or ethylene- α -olefin
20 copolymer made by a metallocene catalyst. As a specific embodiment of the present invention, the metallocene-made polyethylene is a low density polyethylene, more specifically a copolymer of ethylene with an alpha olefin comonomer having from 4-12 carbon atom. As a more specific embodiment of the present
25 invention, a ethylene/1-octene copolymer(s), ethylene/1-propene/1-octene terpolymer(s), and mixture thereof, made by a metallocene catalyst is used. As a still more specific embodiment of the present invention, a metallocene-made low density polyethylene purchased from Dow Chemical Company
30 identified as Affinity FM 1570, which is an ethylene-octene copolymer, is used as the parent thermoplastic. As another still more specific embodiment of the present invention, a metallocene-made low density polyethylene purchased from Dow Chemical Company identified as Affinity PL 1850, which is an ethylene-octene
35 copolymer, is used as the metallocene-made low density polyethylene.

Metallocene catalysts, also referred to as constrained geometry catalysts, are characterized as having a single, stable chemical type rather than a volatile mixture of states as discussed for conventional Ziegler-Natta catalysts. This results
5 in a system composed of catalyst positions which have a singular activity and selectivity. For this reason, metallocene catalyst systems are often referred to as "single site" owing to the homogeneous nature of them, and polymers and copolymers produced from them are often referred to as single site resins by their
10 suppliers.

Generally speaking, metallocene catalysts are organometallic compounds comprising a metal coordination complex comprising a metal of groups 3-10 or the Lanthanide series of the Periodic Table of the Elements, preferably a metal of groups 3-6,
15 and especially a metal of groups 4 and 5, such as hafnium, titanium, vanadium, or zirconium, and a delocalized pi-bonded moiety substituted with a constrain-inducing moiety, such as one or more cyclopentadienyl ligands. A cocatalyst, such as but not limited to, oligometric methyl alumoxane is often used to promote
20 the catalytic activity. By varying the metal component and the cyclopentadienyl ligand a diversity of polymer products may be tailored having molecular weights ranging from about 200 to greater than 1,000,000 and molecular weight distribution from 1.5 to about 15. The choice of co-catalyst influences the efficiency
25 and thus the production rate, yield, and cost.

Exxon Chemical in U.S. Patent 4,701,432 sets out examples of which olefin catalyst systems are of the metallocene class and which are non-metallocene. They cite
30 bis(cyclopentadienyl) dichloro-transition metal, bis(cyclopentadienyl)methyl, chloro-transition metal, and bis(cyclopentadienyl)dimethyl-transition metal as examples of metallocene catalysts, where the metals include choices such as titanium, zirconium hafnium, and vanadium. The patent further provides examples of non-metallocene catalysts as being $TiCl_4$,
35 $TiBr_4$, $Ti(OC_4H_9)_2Cl_2$, VC_{14} , and $VOCl_3$.

As a consequence of the single site system afforded by metallocenes, olefinic copolymers, such as ethylene/alpha-olefin

copolymers, can be produced with each polymer chain having virtually the same architecture. Therefore, the copolymer chains produced from single site systems are uniform not only in chain length, but also in average comonomer content, and even
5 regularity of comonomer spacing, or incorporation along the chain.

In contrast to Ziegler-Natta catalyst made polymers, these single site metallocene polymers are characterized as having a narrow MWD and narrow compositional distribution (CD).
10 While conventional polymers have MWD's of about 3.5 to 8.0, metallocene-made polymers range in MWD from about 1.5 to about 2.5 and most typically about 2.0. MWD refers to the breadth of the distribution of molecular weights of the polymer chains, and is a value which is obtained by dividing the number-average
15 molecular weight into the weight-average molecular weight. The low CD, or regularity of side branches chains along a single chain and its parity in the distribution and length of all other chains, greatly reduces the low MW and high MW "tails". These features reduce the extractables which arise from poor LMW
20 control as well as improve the optics by removing the, e.g. linear, ethylene-rich portions which are present in conventional heterogeneous resins.

Thus, conventional Ziegler-Natta systems produce heterogeneous resins which reflect the differential character of
25 their multiple catalyst sites while metallocene systems yield homogeneous resins which, in turn, reflect the character of their single catalytic site.

Another distinguishing property of single site catalyzed ethylene copolymers is manifested in their melting
30 point range. The narrow CD of metallocenes produces a narrow melting point range as well as a lower Differential Scanning Calorimeter (DSC) peak melting point peak. Unlike conventional resins which retain a high-melting point over a wide density range, metallocene resin melting point is directly related to
35 density. For example, an ethylene/butene-1 copolymer having a density of 0.905 g/cc produced using a metallocene catalyst has a peak melting point of about 100°C, while a slightly lower

density ethylene/butylene copolymer which was made using a conventional Ziegler catalyst reflects its heterogeneous nature with a melting point at about 120°C. DSC shows that the Ziegler resin is associated with a much wider melting point range and
5 actually melts at higher temperatures despite its lower density.

In recent years, several resin suppliers have been researching and developing metallocene catalyst technology. The following are patent literature disclosing none-limiting illustrative examples of metallocene catalysts which are suitable
10 for use in preparing the thermoplastics of the present invention and processes of preparing metallocene-made thermoplastics, the teaching of which are incorporated herein by reference.

Dow in EP 416,815 disclosed the preparation of ethylene/olefin copolymers using monocyclopentadienylsilane complexed of a transition metal. The homogeneous ethylene
15 copolymers which may be prepared using this catalyst are said to have better optical properties than typical ethylene polymers and be well suited for film or injection molding.

Wellborn in Exxon U.S. 4,306,041 discloses the use of metallocene catalysts to produce ethylene copolymers which have
20 narrow molecular weight distributions.

Chang, in Exxon U.S. 5,088,228 discloses the production of ethylene copolymers of 1-propene, 1-butene, 1-hexene, and 1-octene using metallocene catalysts.

Exxon in U.S. 4,935,397 discloses the production of ethylene copolymers using metallocene catalysts to manufacture
25 polymer suitable for injection molding or thermoforming.

Wellborn, in Exxon U.S. 5,084,534 discloses the use of bis(n-butylcyclopentadienyl)zirconium dichloride to produce high
30 molecular weight polyethylene having a polydispersity of 0.8 and a density of 0.955/cc.

In Exxon U.S. 3,161,629 a cyclopentadienyl complex is disclosed which may be used to produce polyolefins having controlled molecular weight and density suitable for use in
35 extrusion of injection molding.

Canich in Exxon U.S. 5,055,438 and 5,057,475 discloses the use of mono-cyclopentadienyl catalysts having a unique

silicon bridge which may be employed to select the stereochemical structure of the polymer. Catalysts such as methyl, phenyl, silyl, tetramethylcyclopentadienyl-terbutylamido-zirconium dichloride may be used to produce polyethylene and ethylene copolymers suitable for films and fibers.

Mitsui Toatsu in JP 63/175004 employed bis(cyclopentadienyl)ethoxy-ZrCl₂ to prepare homogeneous ethylene copolymers.

Mitsubishi in JP 1,101,315 discloses the use of bis(cyclopentadienyl)ZrCl₂ for the preparation of ethylene butene copolymers.

Dow Chemical in WO 93/13143 discloses an ethylene/alpha-olefin interpolymer products comprising a first homogeneous ethylene polymer, specifically a copolymer of ethylene and 1-octene, made with a titanium metallocene catalyst and a second homogeneous ethylene/alpha-olefin copolymer, specifically a copolymer of ethylene and 1-octene, made with a zirconium metallocene catalyst.

As one specific embodiment of the present invention, the metallocene-made polyethylenes are polyethylenes produced by polymerizing ethylene with an alpha-olefin having from 4 to 12 carbon atoms, optionally one or more other alpha-olefin(s) having from 3 to 12 carbon atoms, in the presence of metallocene catalysts which achieve a density from 0.860 to 0.930, particularly from about 0.860 to about 0.920, a molecular weight distribution of less than 4, particularly less than 3, and good distribution of ethylene and from about 0% to about 40%, particularly from about 8% to about 30%, by weight of an alpha-olefin comonomer having from 4 to 12 carbon atoms, and optionally from about 0% to about 40% by weight of one or more other alpha-olefin(s) having from 3 to 12 carbon atoms such as propylene. The metallocene-made polyolefins are produced as described in U.S. Patent Nos. 5,322,728 and 5,272,236 which descriptions are incorporated by reference herein. Such metallocene polyolefins are available from Dow Chemical Company under the trademarks ENGAGE and AFFINITY (ethylene/octene copolymers) and from EXXON Chemical Company under the trademark EXACT (ethylene/butene copolymers).

The polymerization process for making the metallocene-made thermoplastics may be accomplished, although not limited to, at conditions well known in the prior art for Ziegler-Natta or Kaminsky-Sinn type polymerization reactions, that is, 5 temperatures from 0 to 250°C and pressures from atmospheric to 1000 atmospheres (100 MPa). Suspension, solution, slurry, gas phase or other process conditions may be employed if desired. A support may be employed but preferably the catalysts are used in a homogeneous manner. It will, of course, be appreciated that 10 the active catalyst system, especially nonionic catalysts, form in situ if the catalyst and the cocatalyst components thereof are added directly to the polymerization process and a suitable solvent or diluent, including condensed monomer, is used in said polymerization process. It is, however, preferred to form the 15 active catalyst in a separate step in a suitable solvent prior to adding the same to the polymerization mixture.

The metallocene-made thermoplastic polymers usable herein can be either homopolymers or copolymers. If copolymers are used, they can be binary copolymers, ternary copolymers or 20 terpolymers, or copolymers with 4 or more monomers; they can be random or block copolymers. As a specific embodiment of the present invention, polyethylene useful in the present invention have a melt index of less than 60, more specifically from about 0.1-15, as measured by ASTM D-1238, condition E at 190°C.

25 Metallocenes make polymers with uniform, narrow molecular weight distribution (MWD), high comonomer content, relatively even comonomer distribution and an enormously wide choice of comonomers, compared to multi-site Ziegler-Natta catalysts.

30 The poly-1-butene usable herein is a homopolymer or copolymer containing more than 50 mole% butene-1 having a melt index of from about 0.05 to about 300, specifically from about 0.1 to about 40, and more specifically from about 0.4 to about 10 dg/min., as determined by ASTM D-1238 condition E, at 190°C.

35 As a specific embodiment of the present invention, the polybutylene referred to herein is a butene-1 polymer containing from 90% preferably from 95% and more preferably from 97% by

weight of stereospecific portions. These stereospecific portions can be either isotactic or syndiotactic. As an illustrative example, isotactic poly-1 butenes having a low molecular weight, e.g. about 280,000 as determined by solution viscosity in
5 "Decalin" (decahydronaphthalene) may be used. A butene-1 polymer (PB) usable herein is either a butene-1 homopolymer or a copolymer or a terpolymer. If a butene-1 copolymer is used, the non-butene comonomer content is from 1 to 50%, preferably from 1 to 30 mole% of either ethylene, propylene, or an alpha olefin
10 having from 5 to 8 carbon atoms. The poly-1-butenes can be modified to increase surface activity by reaction with, for example, maleic anhydride.

Suitable poly-1-butenes can be obtained in accordance with polymerization of butene-1 with catalysts of halides of
15 Groups IV-VI metals, e.g. titanium, vanadium, chromium, zirconium, molybdenum and tungsten, etc. and cocatalysts of metal alkyl compounds, specifically, Ziegler-Natta catalysts of titanium halides or vanadium halides with aluminum halides or aluminum alkyl (halides) compounds. As a specific examples, the
20 poly-1-butene can be obtained by a low-pressure polymerization of butene-1, e.g. by polymerizing butene-1 with catalysts of $TiCl_3$ or $TiCl_3-AlCl_3$ and $Al(C_2H_5)_2Cl$ at temperatures of 10-100°C, preferably 20-40°C, or $TiCl_3-AlCl_3$ and $Al(C_2H_5)_2Cl$ at temperatures of 10-100°C, preferably 20-40°C, e.g. according to the process
25 described in DE-A-1,570,353 or U.S. Pat. No. 3,197,452. High melt indices are obtainable by further processing the polymer by peroxide cracking, thermal treatment or irradiation to induce scissions leading to a higher melt flow material.

Suitable poly-1-butenes can also be obtained using a
30 high activity Ziegler-Natta catalyst of magnesium supported $TiCl_4$, with organoaluminum or $AlCl_3$ cocatalyst. It can be polymerized by a gas phase, liquid phase, suspension, solution phase, or slurry polymerization process.

Duraflex® PB 0110, a polybutylene polymer produced by
35 Shell Chemical Company, of Houston, Texas is a particularly suitable polymer. This polymer is a homopolymer with a melt

index of 0.4 g/10 min. at 190°C and a molecular weight of about 800,000.

A preferred blend uses about 15-25 wt% of a butene-1 polymer having a melt index equal to 0.4-10 dg/min. (ASTM 1238 condition E), and 20-45 wt% of a metallocene-made polyethylene, e.g. an low density ethylene-octene copolymer such as Affinity PL1850, and 55-70 wt% LDPE of such as LDPE 2500 or LDPE 2500 FA.

Blending of the components can occur by, for example, dry tumble blending, masterbatch, or melt compounding techniques. The method of combining the ingredients of the formulation is important. For example, in most cases, it is desirable to use the least amount of energy to merge the components into an effective blend. Therefore, the preferred method of blending is dry blending the component.

The novel polymer mixtures may be formed into an oriented or unoriented film by casting or film blowing method. After fabrication, the film can be heat sealed by sealing jaws at a preset temperature, pressure, and dwell. The seal strength is tested by an Instron tensile tester at 10"/min. crosshead speed. Maximum strength on a one inch width strip was designated as peel seal strength.

These manufacturing techniques are applicable to film making, although this invention may also be applied to sheet making. Films refer to shaped plastics that are comparatively thin and have maximum thickness of about 0.010 inches (10 mils). Sheets are shaped plastics having thickness greater than 0.010 inches.

The present invention also relates to the peel seal coating layer of a laminated structure comprising a backing material and said peel seal coating. The peel seal coating, which consists of a blend of the present invention can be coated or laminated onto a desired backing material. The backing material can be a member of the group consisting of, but not limited to poly-4-methyl pentene, nylon, high density polyethylene, aluminum foil, polycarbonate, polystyrene, polyurethane, polyvinyl chloride, polyester, polyacrylonitrile, and polypropylene. Except for high density polyethylene, nylon

and the aluminum foil, the remaining backing material may require a tie layer adhesive for use with the novel film layer.

5 The laminated structure can be made by making two separate films that are then laminated. The films may be prefabricated by either film blowing (melt extrusion with a circular die) or the casting method (a flat die-melt extrusion process).

10 The resultant film article can be prepared by any suitable means, such as heat lamination or coextrusion. Coextrusion techniques that can be used for the preparation of the instant film include those described in details in U.S. Pat. No. 2,480,998.

15 Melt extrusion with a flat die (casting) may be accomplished for the present blends by using a flat die or slot die. The extrusion process starts with the present blends in a form that can be fed continuously into an extruder by means of a screw or pneumatic tube. Sometimes, the polymers are combined with materials such as plasticizers, lubricants, (anti-)slip agents, anti-blocking agents, stabilizers, and colorants by means of Banbury mixers. The resulting mix is extruded through rod shaped dies and chipped into pellets. Pelletized polymer is fed into a screw conveyor into the end of screw-type extruder and is heated and made into viscous fluid in a cylinder by means of a revolving, helical screw. The sheet emitting from the die is 25 quenched on a temperature controlled chill roll. Finished films may be subject to a two-way stretching using continuous tenterframe operation in biaxial orientation.

As used herein, the word "comprises" means "including the following elements but not excluding others."

30 The invention will be illustrated by the following illustrative embodiments which are provided for illustration purpose only and are not intended to limit the scope of the instant invention.

ILLUSTRATIVE EMBODIMENT I

35 Blends were prepared by dry blending in a tumbler mixer the following three ingredients; (i) LDPE 2500 or LDPE 2500FA available from Shell Chemical Company in London, England; (ii)

Affinity PL1845, an ethylene-octene copolymer of a density of about .910 gm/cc (ASTM D-1238) made by metallocene, available from Dow Chemical Company, and (iii) Duraflex® PB0110 poly-1-butene homopolymer, available from Shell Chemical Company, Houston, Texas, having a melt index of about 0.4 dg/min. (ASTM method D-1238 condition "E") and a density of about 0.9. The resultant blends were each coextruded with Hoechst-Celanese 7740 high density polyethylene (HDPE) at a die temperature of about 210°C. into films of about 2.5 mils in thickness using a flat die. The films each comprised 2.0 mils of HDPE and 0.5 mils of the remaining components. Hot tack strengths were tested. Film samples of each composition of one inch wide and 12 inches long were tested at temperatures of 90, 100, 110, 120 and 130 °C. Hot tack strengths were determined using a DTC Hot Tack Tester using 40 psi seal bar pressure, 150 mm/sec peel speed, 0.5 seconds dwell time and 0.3 seconds delay time setting. Hot tack strengths for the films, and the compositions of the films are provided in TABLE I.

TABLE I					
HOT TACK STRENGTH OF PB-LDPE-mLDPE BLENDS					
Blends Compositions	Hot Tack Strength (N/INCH)				
Sealing Temperature, °C	90	100	110	120	130
80% LDPE + 20% PB (Control)	0.16	0.359	0.955	0.739	0.7
60% LDPE + 20% PB + 20% mLDPE	0.141	0.408	1.478	1.199	2.245
40% LDPE + 20% PB + 40% mLDPE	0.233	1.203	2.861	2.652	2.814
20% LDPE + 20% PB + 60% mLDPE	0.164	1.697	2.956	2.924	2

As may be seen from TABLE 1, the films made from various blends of the present invention and the control blend(PB and LDPE) were tested for hot tack strength in Newtons per inch at sealing temperatures of 90, 100, 110, 120, and 130°C. It has been unexpectedly found that the addition of a metallocene-made polyethylene, specifically AFFINITY PL 1845 (an ethylene-octene low density copolymer made by metallocene), to a blend of polybutylene and LDPE (both made by a conventional catalyst), when cast, results in a unique film which has significantly improved hot tack strength, good processability (does not adhere to the processing equipment) and will bond by coextrusion or extrusion lamination to a high density polyethylene substrate in

a laminar structure without the need for an adhesive to achieve such bonding.

The properties of Duraflex® PBO110 and AFFINITY PL1845 are listed in TABLE II and TABLE III below.

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TABLE II
DURAFLEX® POLYBUTYLENE 0110

TYPICAL PHYSICAL PROPERTIES*					
Property	ASTM Test Method	English		English	
		Unit	Value	Unit	Value
General properties					
Melt Index	D 1238	--	--		0.4
Density	D 1505	lb/ft ³	58.0	gms/10 min g/cm ³	.915
Mechanical properties					
Tensile strength at yield	D 638	psi	2500	MPa	17.2
Tensile strength at break	D 638	psi	>4000	MPa	>27.6
Elongation at break	D 638	%	>300	%	>300
Modulus of elasticity	D 638	psi	42500	MPa	293
Hardness, Shore	D 2240	D Scale	D 60	D Scale	D 60
Thermal properties					
Melting point range	DTA	F	225-229	C	124-126
Softening point vicat	D 1525	F	235	C	113
Coefficient of expansion	D 696	In/in F	7.1 x 10 ⁻⁵	cm/cm/ C	1.3x10 ⁻⁴
Thermal conductivity (70 F) (21 C)	C 177	Btu/ft ² / Hr/ F/in	1.25	Kcal/m ² /hr/ C/cm	16

*Compression molded specimen conditioned, 10 days at 73°F (22.8 C).

TABLE III
AFFINITY PL1845
Polyolefin Plastomer

Physical Properties	Method	Test	Values ¹
Percent Comonomer, octene	Dow ²		9.5
Melt Index, dg/min	ASTM D-1238		3.5
Density, gm/cc	ASTM D-792		.910
DSC Melting Point, F (C)	Dow		217 (103)
Dow Rheology Index (DRI)	Dow ³		1.4
Cast Film Properties, 1.0 mil (25.4 microns)⁴			
Puncture Resistance, ft-lb/in ² (J/cm ²)	Dow		218 (18)
Dart Impact, g (Method B)	ASTM D-1709		470
Elmendorf Tear Strength, g	ASTM D-1709		178
(Type A)	ASTM D-1922		362
Ultimate Tensile, psi (MPa)	ASTM D-882		6,580 (45.4)
	ASTM D-882		4,847 (33.4)
Ultimate Elongation, %	ASTM D-882		527
	ASTM D-882		664
Clarity	ASTM D-1746		75
Gloss, 20	ASTM D-2457		145
Haze, %	ASTM D-1003		0.7
Seal Initiation Temp. F (C)	Dow		210 (99)
¹ These are typical properties only and are not to be regarded as sales specifications.			
² Based on ASTM D-2238, Method B.			
³ A calculated value based on complex viscosity that expresses the relative influence of long chain branching on the extrudability of homogeneous (single site catalyst) polyolefins.			
⁴ Cast film extruded at 525 F (274 C), 20 mil (0.5 mm) die gap.			
⁵ Temperature at which 2 lb/in (8.9N/25.4 microns) heat seal strength is achieved.			

ILLUSTRATIVE EMBODIMENT II (Prophetic)

Blends would be prepared by dry blending in a tumbler mixer the following three ingredients; (i) DuPont Alathon® 3159 ethylene-vinyl acetate copolymer (EVA) available from the DuPont Company in Wilmington, Delaware, (ii) Affinity PL1845, an ethylene-octene copolymer of a density of about .910 gm/cc (ASTM D-1238) made by metallocene, available from Dow Chemical Company, and (iii) Duraflex® PB0110 poly-1-butene homopolymer, available from Shell Chemical Company, Houston, Texas, having a melt index of about 0.4 dg/min. (ASTM method D-1238 condition "E") and a density of about 0.9. The resultant blends are each to be coextruded with Hoechst-Celanese 7740 high density polyethylene (HDPE) at a die temperature of about 210°C. into films of about 2.5 mils in thickness using a flat die. The films each would comprise 2.0 mils of HDPE and 0.5 mils of the remaining components. Hot tack strengths are to be tested. Film samples of each composition of one inch wide and 12 inches long are to be tested at temperatures of 90, 100, 110, 120 and 130 °C. Hot tack strengths are to be determined using a DTC Hot Tack Tester using 40 psi seal bar pressure, 150 mm/sec peel speed, 0.5 seconds dwell time and 0.3 seconds delay time setting.

The films which would be made from various blends of this Embodiment and the control (PB and EVA) would be tested for hot tack strength in Newtons per inch at sealing temperatures of 90, 100, 110, 120, and 130°C. It would be unexpectedly found that the addition of a metallocene-made polyethylene, specifically AFFINITY PL 1845 (an ethylene-octene low density copolymer made by metallocene), to a blend of polybutylene and polyethylene vinyl acetate, when cast, would result in a unique film having significantly improved hot tack strength, good processability (does not adhere to the processing equipment) and would bond by coextrusion or extrusion lamination to a high density polyethylene substrate in a laminar structure without the need for an adhesive to achieve such bonding.

The ranges and limitations provided in the instant specification and claims are those which are believed to particularly point out and distinctly claim the instant

invention. It is, however, understood that other ranges and limitations that perform substantially the same function in substantially the same manner to obtain the same or substantially the same result are intended to be within the scope of the
5 instant invention as defined by the instant specification and claims.

CLAIMS

1. A packaging film or sheet, capable of forming peel seals suitable for vertical form/fill/seal packaging, which is made from a blend comprising:

5 (i) from about 15 wt.% to about 85 wt.% of an ethylene polymer made by a conventional catalyst;

(ii) from about 10 wt.% to about 70 wt.% of a metallocene-made polyethylene;
and

10 (iii) from about 5 wt.% to about 55 wt.% of a butene-1 homopolymer or copolymer, based on the total weight of said blend.

2. The film or sheet as described in claim 1, wherein the peel seal strength of said film or sheet is from about 0.5 to
15 about 8.0 pound per inch, and the hot tack strength is from 1.0 to about 4.0 Newton/15 mm. .

3. The blend as described in claim 1, wherein said ethylene polymer is polyethylene made by a Ziegler-Natta catalyst.

4. The blend as described in claim 1, wherein said ethylene
20 polymer is an ethylene unsaturated ester copolymer.

5. The blend as described in claim 3, wherein said ethylene polymer is a LDPE, and said metallocene-made polyethylene is an ethylene-octene polymer.

6. The blend as described in claim 4, wherein said ethylene
25 polymer is an ethylene-vinyl acetate copolymer, and said metallocene-made polyethylene is an ethylene-octene polymer.

7. A laminate structure suitable for vertical form/fill/seal packaging comprising a backing material to which is bonded a film or sheet, capable of forming peel seals, which is made from a
30 blend comprising:

(i) from about 15 wt.% to about 85 wt.% of an ethylene polymer made by a conventional Catalyst;

(ii) from about 10 wt.% to about 70 wt.% of a metallocene-made polyethylene;
35 and

(iii) from about 5 wt.% to about 55 wt.% of a butene-1 homopolymer or copolymer; based on the total weight of said blend.

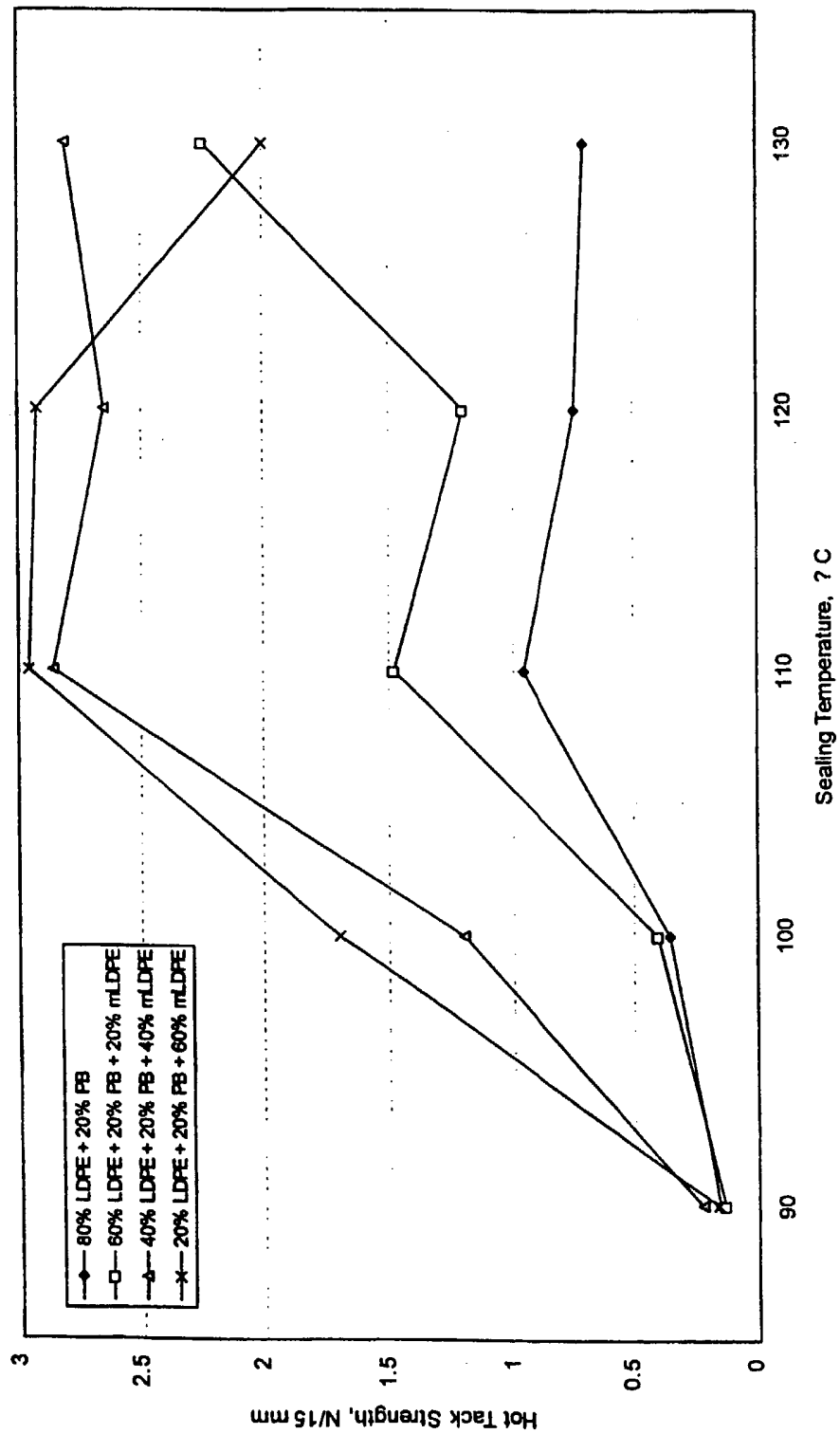
8. The laminate as described in claim 7, wherein the peel seal strength of said film or sheet is from about 0.5 to about 8.0 pound per inch, and the hot tack strength is from 1.0 to about 4.0 Newton/15 mm.

9. The laminate as described in claim 8, wherein said ethylene polymer is a LDPE, made by a Ziegler-Natta catalyst, and said metallocene-made polyethylene is an ethylene-octene polymer.

10. The laminate as described in claim 8, wherein said ethylene polymer is an ethylene-vinyl acetate copolymer made by a Ziegler-Natta catalyst, and said metallocene-made polyethylene is an ethylene-octene polymer.

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HOT TACK STRENGTH OF PB-LDPE-mLDPE BLENDS



INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 98/27709

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C08L23/16 C08J5/18

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C08L C08J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 97 28960 A (TREDEGAR IND INC) 14 August 1997 see page 9, line 22; example 3; table 1 ---	1,2,4, 6-8,10
Y	EP 0 339 989 A (SHELL OIL CO) 2 November 1989 see page 2, line 58 - page 3, line 43 ---	3,5,9
Y	US 5 508 051 A (FALLA DANIEL J ET AL) 16 April 1996 see column 9, line 6 - column 10, line 31 -----	3,5,9

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

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INTERNATIONAL SEARCH REPORT

Information on patent family members

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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9728960 A	14-08-1997	AU 1344997 A	28-08-1997
EP 0339989 A	02-11-1989	US 4882229 A	21-11-1989
		AT 109814 T	15-08-1994
		AU 3372589 A	02-11-1989
		DE 68917359 D	15-09-1994
		DE 68917359 T	01-12-1994
		DK 209189 A	30-10-1989
		JP 1315443 A	20-12-1989
		JP 2746644 B	06-05-1998
US 5508051 A	16-04-1996	US 5360648 A	01-11-1994
		AU 682526 B	09-10-1997
		AU 7246694 A	17-01-1995
		DE 69413228 D	15-10-1998
		DE 69413228 T	28-01-1999
		EP 0705302 A	10-04-1996
		ES 2123146 T	01-01-1999
		FI 956245 A	22-12-1995
		JP 8511744 T	10-12-1996
		MX 9404784 A	31-01-1995
		NZ 269022 A	24-11-1997
		WO 9500587 A	05-01-1995